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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

ISO/TC 102/SC 2/WG 19B
DETERMINATION OF VANADIUM CONTENT IN IRON ORES BY BPHA SPECTROPHOTOMETRIC METHOD

STATISTICAL ANALYSIS OF INTERNATIONAL TEST DATA - 1986

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(For submission to the Convener of ISO/TC 102/SC 2/WG 19B, to the Secretariat of ISO/TC 102/SC 2 and for presentation at the ISO/TC 102/SC 2 meeting to be held in Tokyo, Japan, 1986-11-10/14)

Project: 30.69.02
Analytical Methodology

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DETERMINATION OF VANADIUM CONTENT IN IRON ORES BY BPHA SPECTROPHOTOMETRIC METHOD

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by

R. Sutarno* and W.S. Bowman**

SUMMARY

The analytical data resulting from the international test on the determination of vanadium in iron ores by BPHA spectrophotometric method conducted by ISO/TC 102/SC 2/WG 19B during the period of 1984-1986 have been statistically evaluated. Based on these analytical results, the precision of the analytical method can be expressed in terms of the V concentration level in the sample by the following equations:

$$r = 0.0344\ X + 0.0016$$
$$P = 0.0689\ X + 0.0010$$
$$sr = 0.0122\ X + 0.0006$$
$$sL = 0.0229\ X + 0.0002$$

where X is the V concentration in the sample, r is the repeatability, P is the permissible tolerance, sr is the within-laboratory standard deviation and sL is the between-laboratories standard deviation all expressed in percent. Six samples containing V ranging from 0.004 to 0.523 percent were used in this international test. Twelve laboratories participated in this test.

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ISO/CT 102/SC 2/GT 19B

DÉTERMINATION DU CONTENU EN VANADIUM DES MINERAIS DE FER PAR LA MÉTHODE SPECTROPHOTOMÉTRIQUE DU BPHA

ÉVALUATION STATISTIQUE DES DONNÉES RÉSULTANT D'UN ESSAI INTERNATIONAL - 1986

par

R. Sutarno* et W.S. Bowman**

RÉSUMÉ

Les données analytiques qui ont résulté d'un essai international effectué dans la période de 1984 à 1986 par le groupe de travail 19B du Sous-comité 102 du Comité technique de l'Organisation internationale de normalisation (ISO) en vue de déterminer la teneur en vanadium des minerais de fer par la méthode spectrophotométrique du BPHA, laquelle utilise le N-benzoyle-phényl-hydroxylamine comme indicateur du vanadium, ont fait l'objet d'une évaluation statistique. Selon ces résultats analytiques, l'estimation de la précision de la méthode peut être exprimée en terme du niveau de concentration du vanadium dans l'échantillon par les équations suivantes:

$$r = 0{,}0344\ X + 0{,}0016$$
$$P = 0{,}0689\ X + 0{,}0010$$
$$sr = 0{,}0122\ X + 0{,}0006$$
$$sL = 0{,}0229\ X + 0{,}0002$$

où "X" représente la concentration en vanadium de l'échantillon, "r", la répétabilité, "P", la tolérance permissible, "sr", l'écart-type de chaque laboratoire et "sL", l'écart-type interlaboratoire, le tout exprimé en pourcentage. Six échantillons dont la concentration en vanadium variait de 0,004 à 0,523 pourcent ont été utilisés aux fins d'essais. Douze laboratoires ont participé à cet essai.

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*Chercheur et **Technologue, Section de la chimie physique, Laboratoire de métallurgie extractive, Laboratoires des sciences minérales, CANMET, Énergie, Mines et Ressources Canada, Ottawa (Ontario), K1A 0G1.

INTRODUCTION

This international test was conducted in accordance with Resolution 15 made at the twelfth meeting of ISO/TC 102/SC 2 held in Paris in 1984 (1). This test was conducted as part of further research on the procedure for obtaining stable colour development and to obtain estimates of the precision of the revised method.

The analytical data were collected by the convener of ISO/TC 102/SC 2/WG 19B (ISO Technical Committee 102 - Iron Ores; Sub committee 2 - Chemical Analyses; Working Group 19B - Determination of vanadium content in iron ore by BPHA spectrophotometric method) from an international test conducted during the period of 1984-1986. Six samples with vanadium contents ranging from 0.004 to 0.523 percent were used. Twelve laboratories provided analytical data; each laboratory analysed two bottles of each sample in duplicate.

The purpose of this statistical evaluation is to provide the working group with the estimates of the precision in the form of repeatability, permissible tolerance, within-laboratory and between-laboratories standard deviations.

PRINCIPLE OF THE ANALYTICAL METHOD (3)

Decomposition of a test portion by fusion or sintering with sodium peroxide and leaching with water and sulphuric acid. Addition of phosphoric acid and potassium permanganate to an aliquot to oxidize vanadium to the quinquevalent state. Reduction of excess permanganate by sodium nitrite in the presence of urea and treatment with n-benzoyl-n-phenylhydroxylamine (BPHA) and hydrochloric acid to form a complex, followed by extraction with chloroform.

Spectrophotometric measurement of the absorbance at approximately 535 nm and comparison with absorbance values of calibration solutions treated in the same manner.

STATISTICAL EVALUATION

The analytical data were statistically evaluated by the procedure described in document ISO/TC 102/TCR 5 (2). This procedure is illustrated schematically in Figure 1.

The raw data and the detailed calculations are presented in Appendix A. They are summarized in Tables 1 and 2. The raw data are also plotted in Figures 2. The boxed points in these figures signify that the data were suspected to be outliers and were excluded from the estimation of the sample means and precisions. The letter C on the boxed points signifies that the data were suspected to be outliers due to poor precision (Cochran's test) and the letter D due to the deviation from the sample means (Dixon's test).

The precisions estimated (sr, sL, r and P) are plotted against their corresponding sample means in Figure 3, and the regression equations of these precisions against sample means were computed and presented in Table 1. Table 2 lists the suspected outliers.

OBSERVATIONS

An ideal standard analytical method is an analytical method that can be applied by any qualified analyst with proper equipment and reagents with equal precision and accuracy. This implies that the better the method is standardized the smaller is the sL/sr ratio and the fewer the number of outliers. The magnitude of within-laboratory standard deviation itself depends on the state of the art of the method. Experience has shown that for a good method, the average sL/sr ratio is found to be about 2. Table 1 shows that the magnitude of the within-laboratory precision seems to be reasonable. Using sL/sr ratio of 2 as a bench mark, the observed sL/sr ratios are acceptable. Table 2 shows that the number of outliers is reasonable, but two laboratories (SE 2 and AU 1) seem to have had some difficulties.

Sample 83-9 was found to be inhomogeneous i.e., the between-bottles variation is significant. For this reason, the mean and precision were estimated from the two-way analysis of variance. As a consequence of this procedure results of IT 1 and JP 1 were excluded because they reported zero

within-bottle variance (see page A.7). Figure 2.2 shows that these results are not the least precise. If the between-bottles variation is ignored, and test for outliers is performed, results reported by SE 2 would be identified as outlier by Cochran's test. This is illustrated in Figure 2.3.

The results of this international test cannot be compared directly with those of previous tests (1982 and 1984), since only two common test samples were used (76-17 and 79-14). Comparison between Table 1 and Table 3 shows that, for these two common samples, there is very little difference between the results of these three international tests. A small difference is that the functional relationships between precision and the concentration level of V in the samples, derived from the results of the present international test, have smaller slopes than those derived from the previous tests. This indicates that the precision is somewhat less dependent on the level of V.

REFERENCES

1. "Final report of the twelfth meeting of ISO/TC 102/SC 2: Iron ores/ Chemical Analysis, Held in Paris, October 16-18, 1984"; ISO/TC 102/SC 2 N792, 1985-03-12.

2. "Procedure for statistical evaluation of analytical data resulting from international tests"; ISO/TC 102/TCR 5, 1985-06-11.

3. "Iron ores - Determination of vanadium content - BPHA spectrophotometric method"; 5th working draft, ISO/TC 102/SC 2/WG 19 (B), November 1985.

Abbreviations Used in this Report

s_r = SIGMA-R - within laboratory standard deviation

s_L = SIGMA-L - between laboratories standard deviation

r* = R - repeatability

$= 2.83\, s_r$

p** = permissible tolerance between laboratories

$= 2.83\left(s_L^2 + s_r^2/2\right)^{\frac{1}{2}}$

* Repeatability, r, is the value below which the absolute difference between two independent single test (analysis) results produced by a laboratory on identical material using the same equipment within a short interval of time, using the standardized test method, may be expected to be with a 95% probability.

** Permissible tolerance between laboratories, P, is the value below which the absolute difference between two means of duplicate test results on identical material obtained by operators of different laboratories using the standardized test method, may be expected to lie with a 95% probability.

KO - total number of participating laboratories

K - number of sets of laboratory results used for ANOVA

NO - total number of analytical results

N - No. of analytical results used for ANOVA

Table 1.

ISO/TC 102/SC 2/WG 19B
DETERMINATION OF VANADIUM CONTENT IN IRON ORES
BY BPHA SPECTROPHOTOMETRIC METHOD

Summary of precision for all samples

Sample	Ko	K	No	N	x	r	P	sr	sL	sL/sr
76-17	12	11	47	43	0.5229	0.0176	0.0357	0.0062	0.0118	1.90
83-9	12	10	48	40	0.3086	0.0159	0.0251	0.0056	0.0079	1.41
85-7	12	10	47	39	0.1042	0.0051	0.0075	0.0018	0.0023	1.29
85-6	12	10	47	38	0.0600	0.0022	0.0027	0.0008	0.0008	0.99
79-14	12	12	47	47	0.0343	0.0038	0.0036	0.0013	0.0008	0.62
83-4	12	12	47	47	0.0106	0.0016	0.0031	0.0006	0.0010	1.72
76-12	12	12	47	47	0.0041	0.0011	0.0013	0.0004	0.0004	0.94

The regression equations are:	Corr. Coeff.
r = 0.0344 X + 0.0016	0.9627
P = 0.0689 X + 0.0010	0.9920
sr = 0.0122 X + 0.0006	0.9629
sL = 0.0229 X + 0.0002	0.9935

Table 2.

ISO/TC 102/SC 2/WG 19B
DETERMINATION OF VANADIUM CONTENT IN IRON ORES
BY BPHA SPECTROPHOTOMETRIC METHOD

List of outliers

Sample	Cochran (Precision)	Dixon (Accuracy)	Lab has only one result	Individual Result (Dixon)
76-17	AU 1	-	-	-
83-9	Sample is Inhomogeneous			
85-7	JP 1	-	-	-
	SE 2	-	-	-
85-6	AU 1	SE 2	-	IT 1
	SE 2	-	-	-
79-14	-	-	-	-
83-4	-	-	-	-
76-12	-	-	-	-

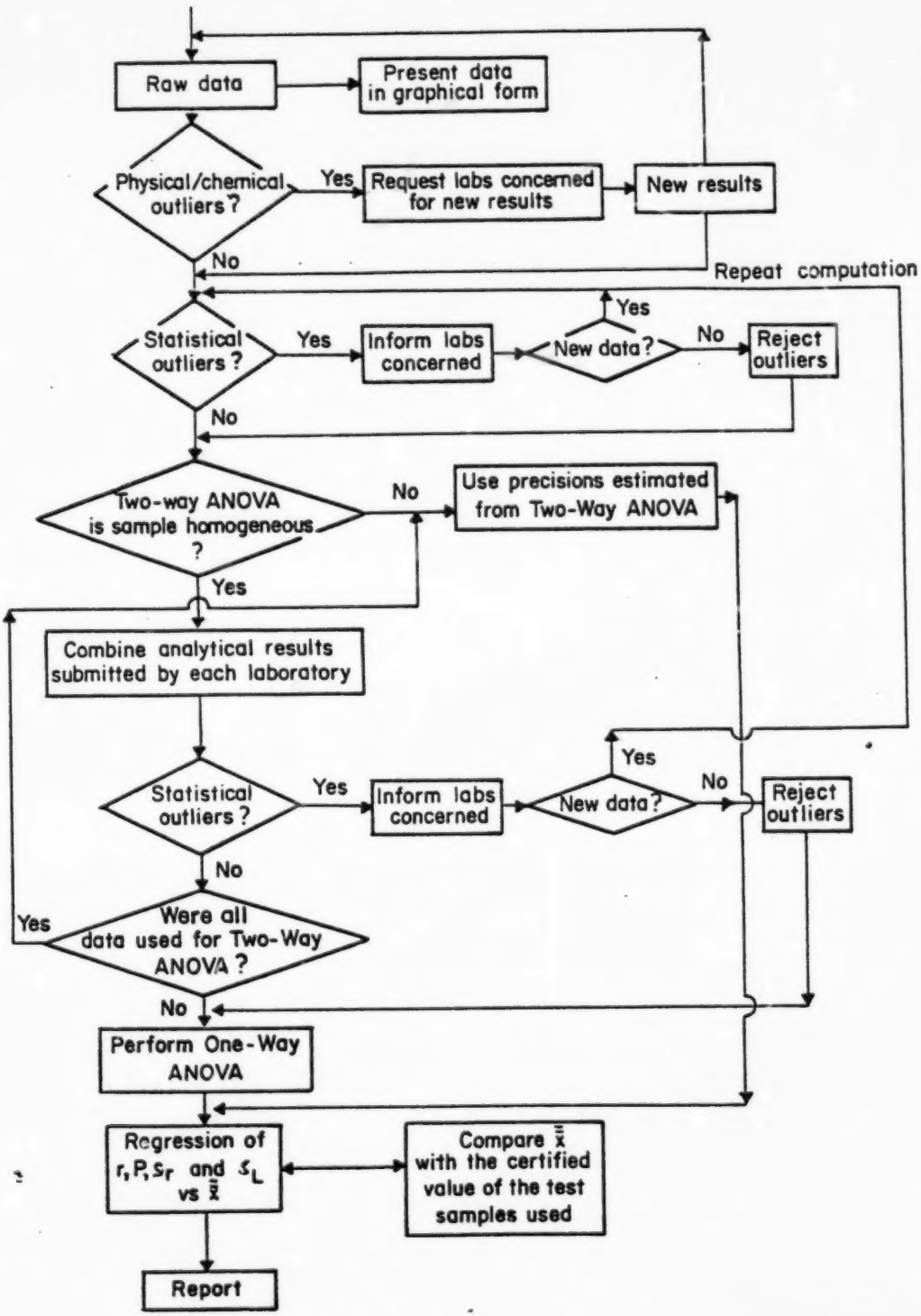

Figure 1. Flow chart of the Procedure for Statistical Evaluation of Analytical Data Resulting from International Tests.

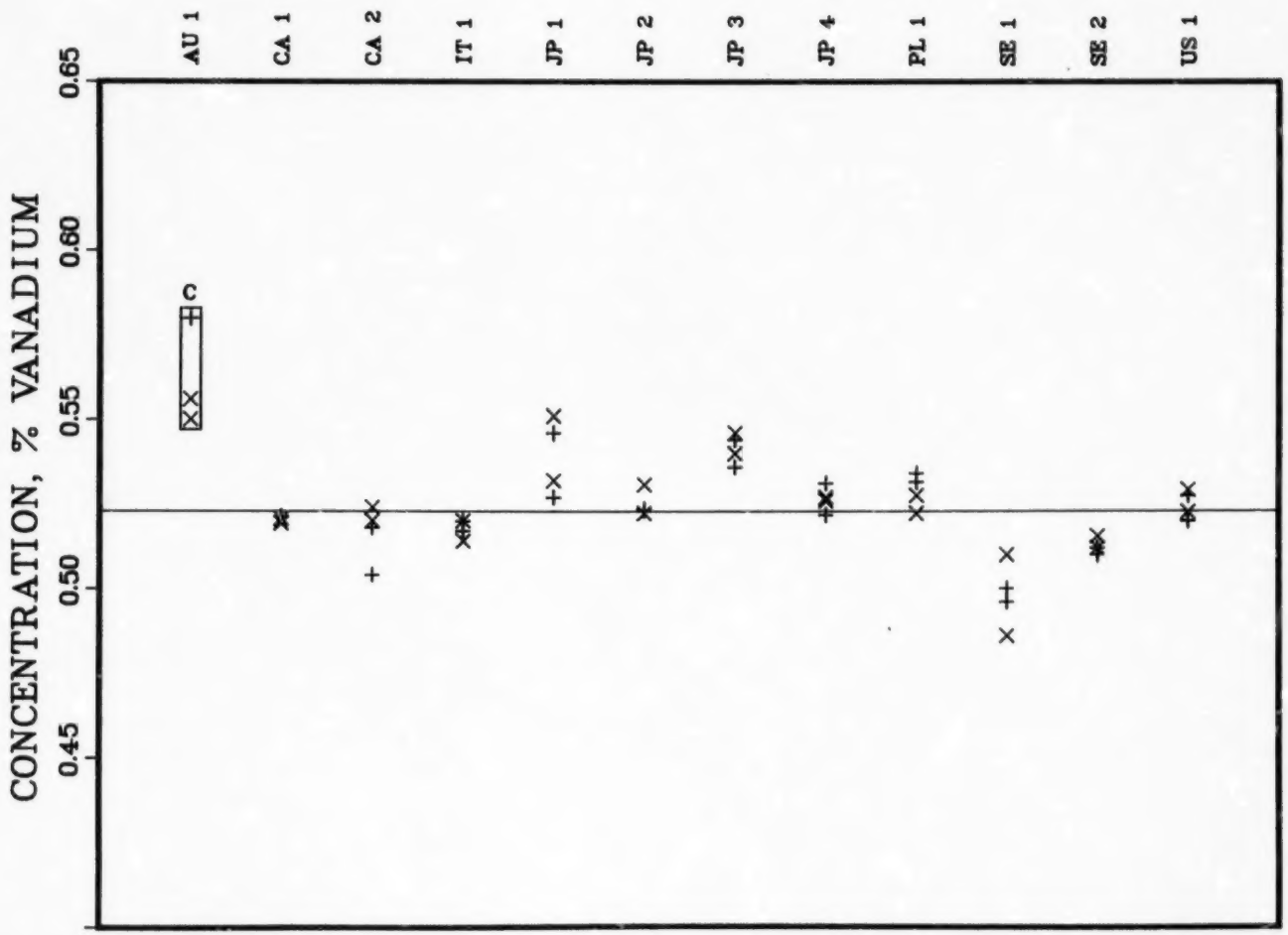

Figure 2.1
ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-17

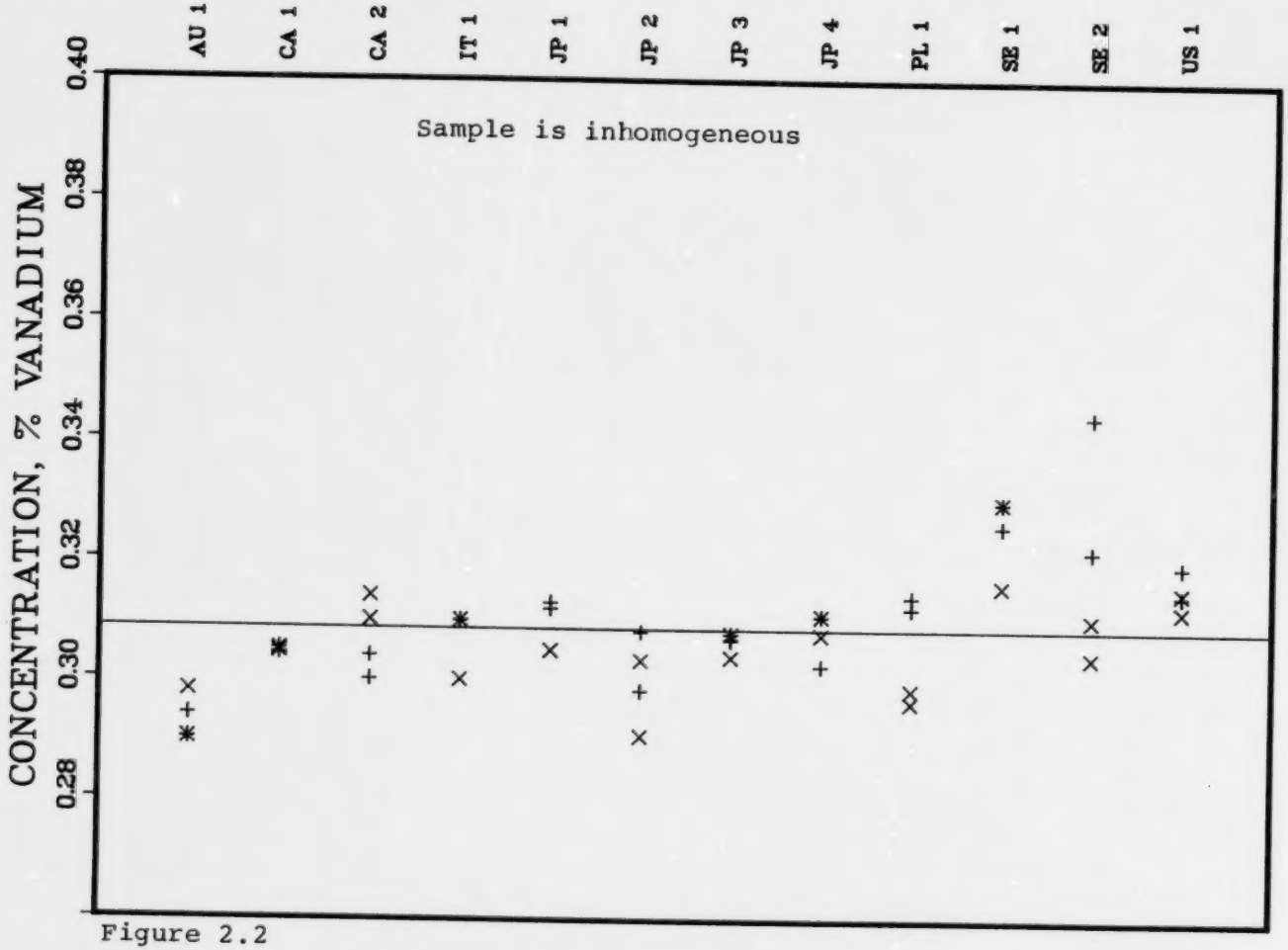

Figure 2.2

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

SAMPLE: 83-9

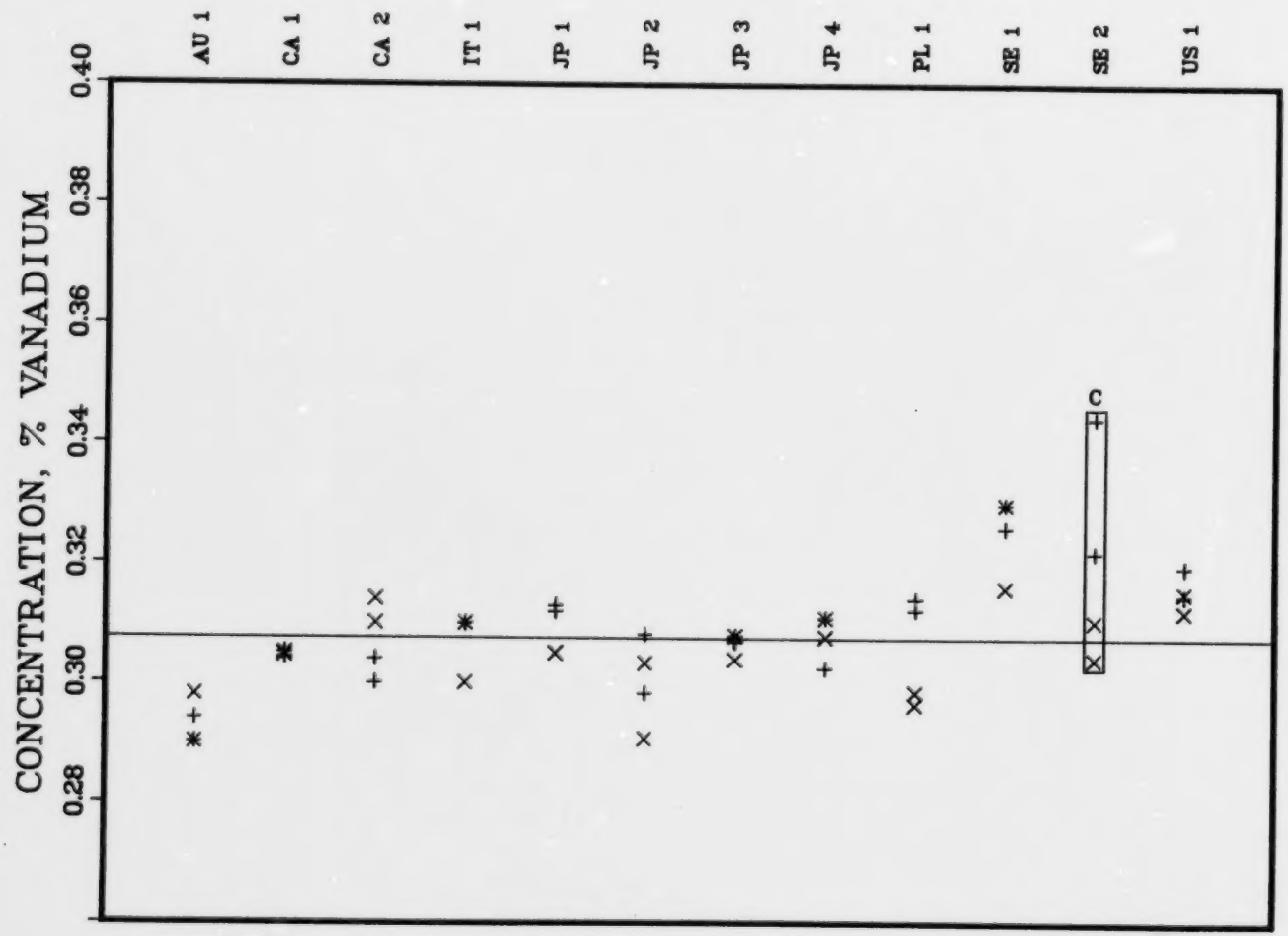

Figure 2.3

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

SAMPLE: 83-9

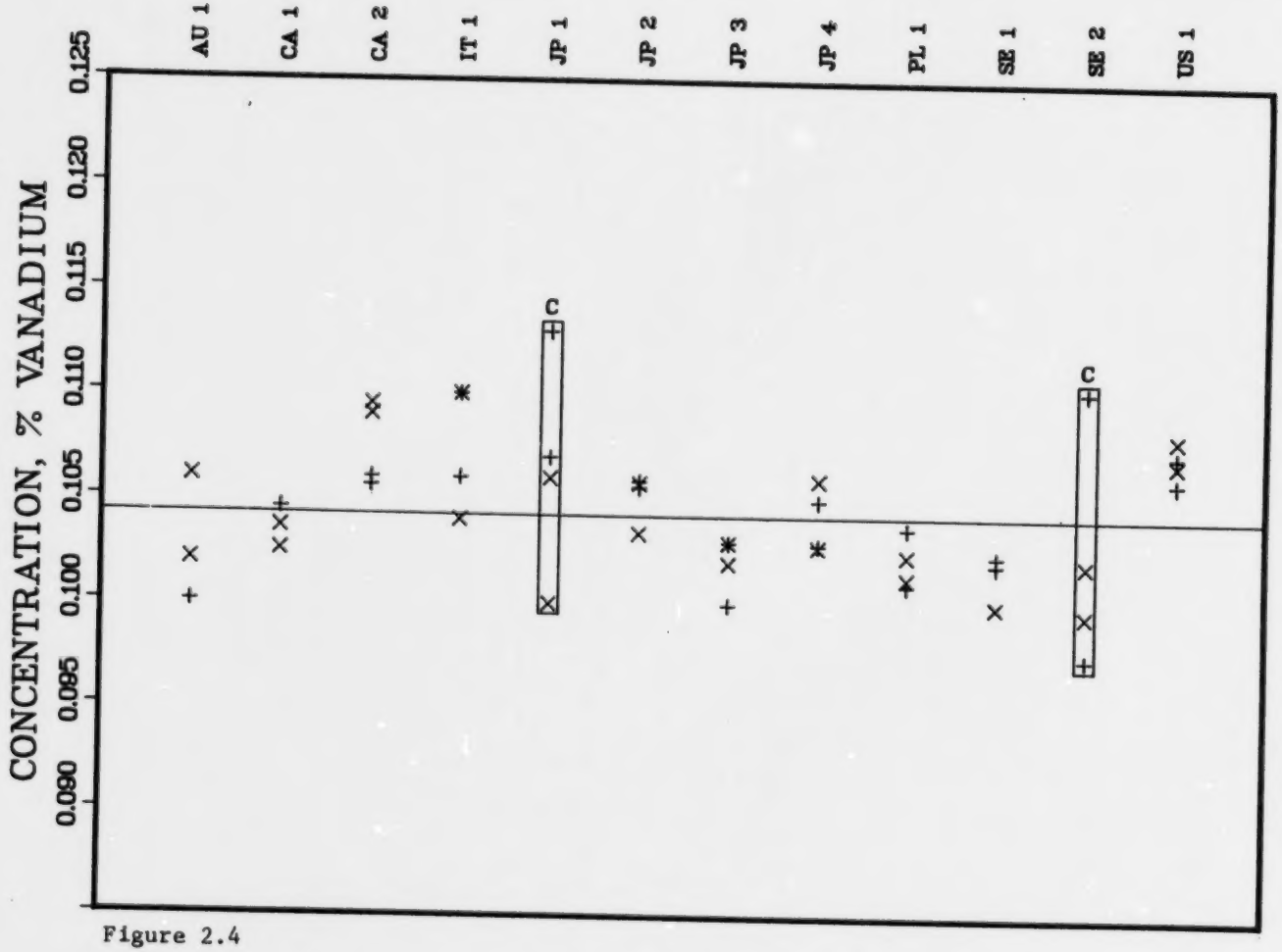

Figure 2.4

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

SAMPLE: 85-7

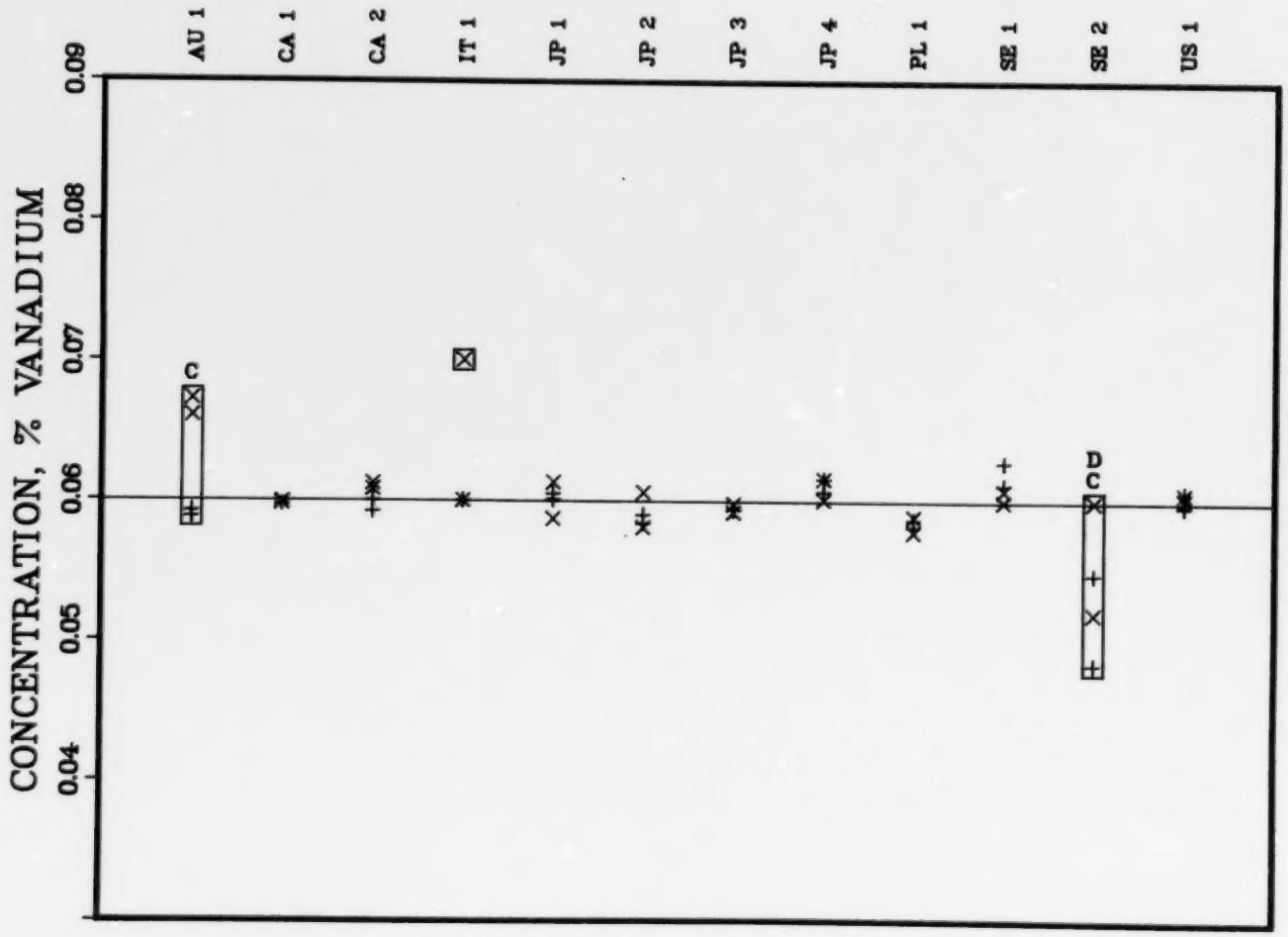

Figure 2.5

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

SAMPLE: 85-6

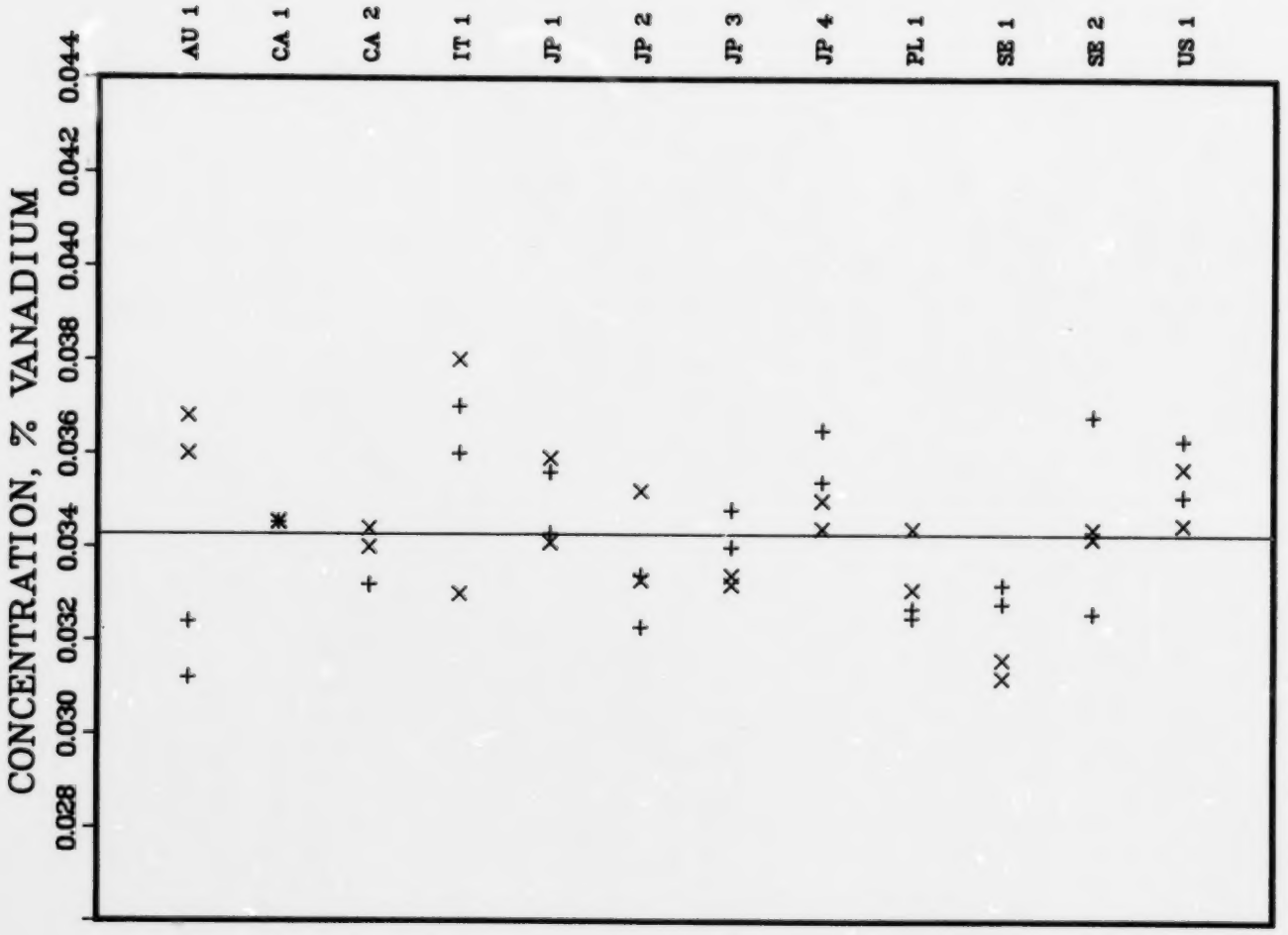

Figure 2.6

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

SAMPLE: 79-14

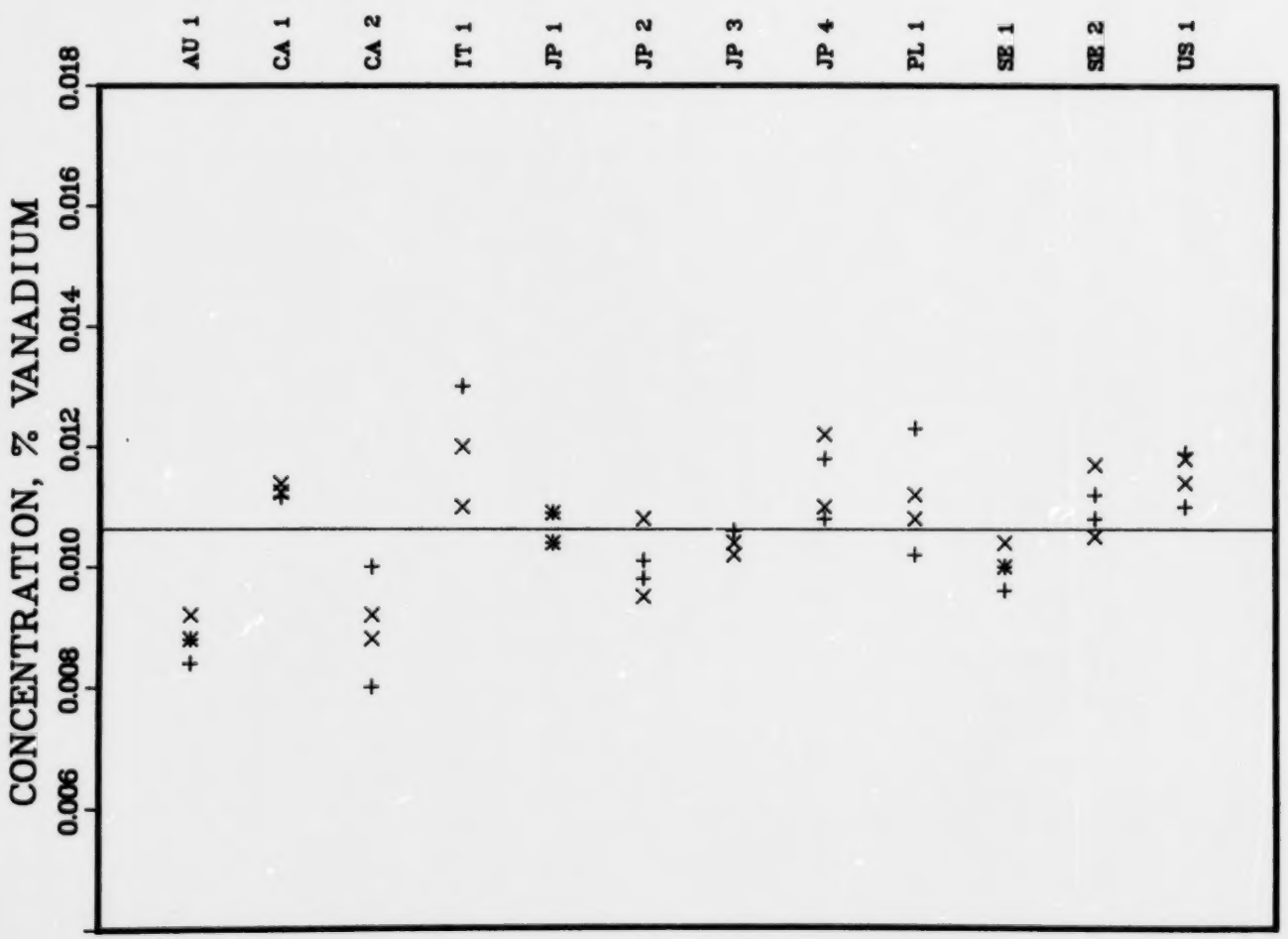

Figure 2.7

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

SAMPLE: 83-4

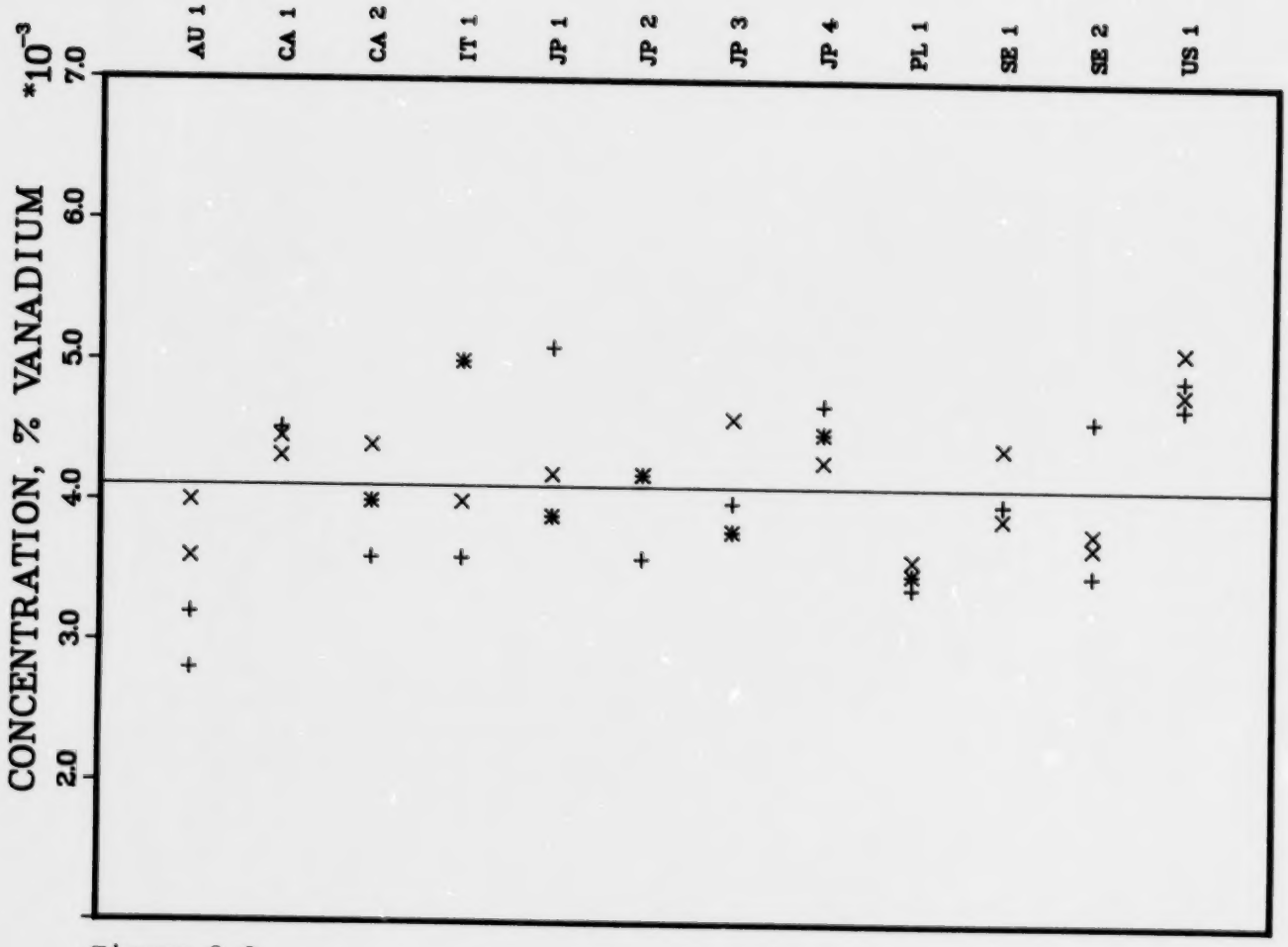

Figure 2.8

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

SAMPLE 76-12

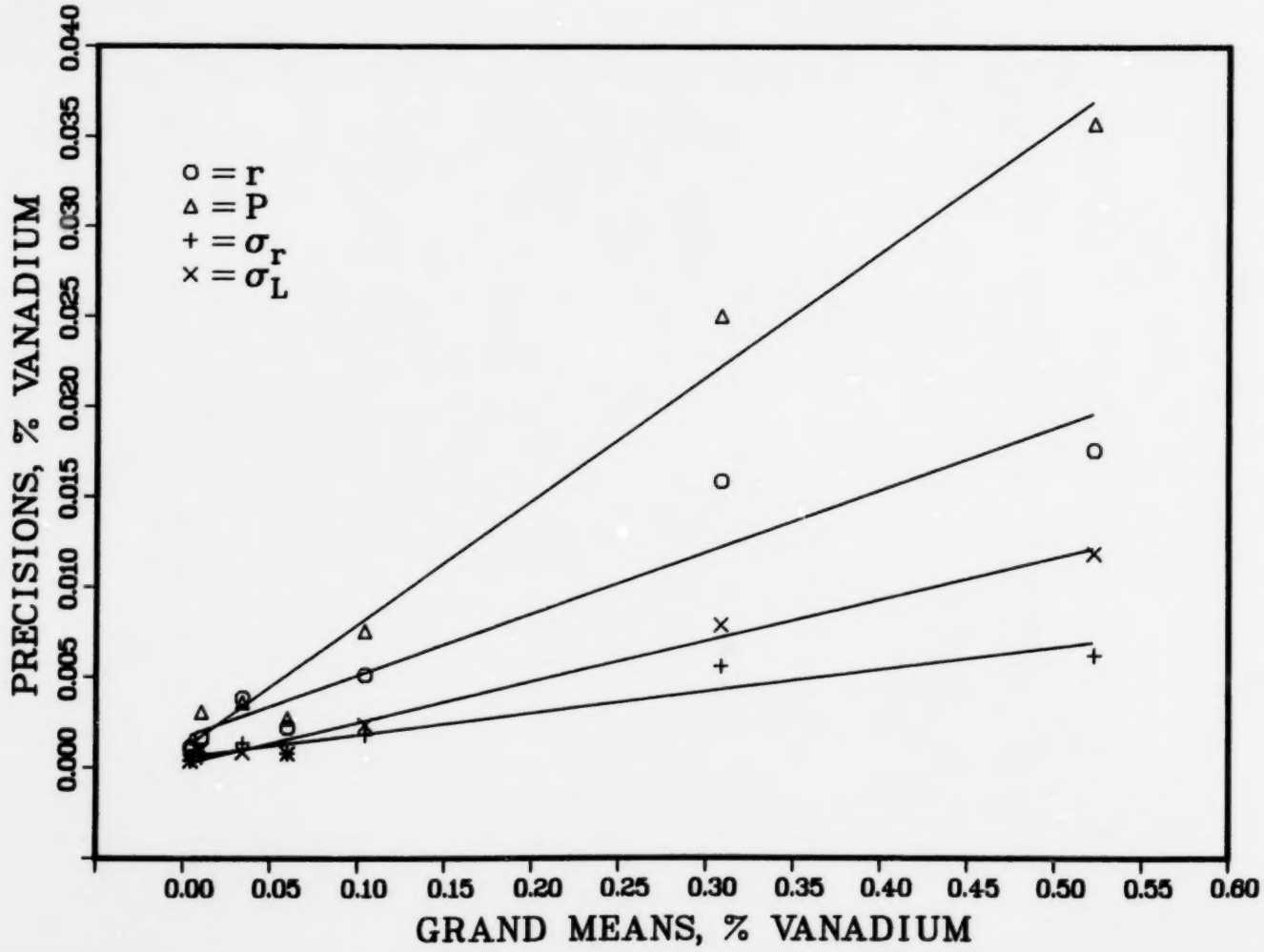

Figure 3

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD

ISO/TC 102/SC 2/WG 19B

DETERMINATION OF VANADIUM CONTENT IN IRON ORES BY BPHA SPECTROPHOTOMETRIC METHOD

STATISTICAL ANALYSIS OF INTERNATIONAL TEST DATA - 1986

APPENDIX A

Detailed Computation of the Analytical Data

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-17

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS VANADIUM		LAB MEAN	LAB VARIANCE
1	AU 1	1	.5500	.5560	.56650	.2490E-03
		2	.5800	.5800		
2	CA 1	1	.5193	.5206	.52040	.1030E-05
		2	.5213			
3	CA 2	1	.5240	.5200	.51650	.7567E-04
		2	.5180	.5040		
4	IT 1	1	.5200	.5140	.51775	.8250E-05
		2	.5170	.5200		
5	JP 1	1	.5320	.5510	.53900	.1287E-03
		2	.5270	.5460		
6	JP 2	1	.5223	.5308	.52498	.1536E-04
		2	.5235	.5233		
7	JP 3	1	.5460	.5400	.54150	.1967E-04
		2	.5440	.5360		
8	JP 4	1	.5260	.5270	.52650	.1489E-04
		2	.5218	.5312		
9	PL 1	1	.5276	.5223	.52893	.2688E-04
		2	.5342	.5316		
10	SE 1	1	.4860	.5100	.49800	.9867E-04
		2	.5000	.4960		
11	SE 2	1	.5120	.5155	.51238	.5229E-05
		2	.5100	.5120		
12	US 1	1	.5226	.5292	.52483	.1818E-04
		2	.5200	.5275		

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-17

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	19.980
CHI-SQUARE(.95,19)	30.148

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS (ALPHA=.05)

AU 1 BOTTLE- 2 T-CALC = 3.887 T-CRIT(.00227,20) = 3.497

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

AU 1	DOORNBOS' TEST FOR BOTTLE MEANS
CA 1	NUMBER OF BOTTLES OR REPLICATES INCORRECT

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-17

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	9	.58421110E-02	.64912344E-03
BETWEEN BOTTLES	10	.24256000E-03	.24256000E-04
WITHIN BOTTLES	20	.99178000E-03	.49589000E-04
TOTAL	39	.70764510E-02	

F-CALC = .489 F-CRIT(.95;10,20) = 2.348

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-17

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	25.115
CHI-SQUARE(.95,11)	19.681

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE (ALPHA=.05)

AU 1 C-CALC = .376 C-CRIT(4,12) = .326

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

AU 1 COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-17

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	10	.58614874E-02	.58614874E-03
WITHIN LABS	32	.12364000E-02	.38637500E-04
TOTAL	42	.70978874E-02	

REPEATABILITY VARIANCE	.38637500E-04
REPEATABILITY STD. DEV.	.00621591
BETWEEN-LABORATORIES VARIANCE	.14013681E-03
BETWEEN-LABORATORIES STD. DEV.	.01183794
REPEATABILITY	.01759102
PERMISSIBLE TOLERANCE BETWEEN LABS	.03573603
GRAND MEAN	.52285116
VARIANCE OF THE GRAND MEAN	.13707157E-04

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-9

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS VANADIUM		LAB MEAN	LAB VARIANCE
1	AU 1	1	.2900	.2980	.29300	.1467E-04
		2	.2900	.2940		
2	CA 1	1	.3046	.3050	.30475	.1367E-06
		2	.3043	.3051		
3	CA 2	1	.3140	.3100	.30700	.3867E-04
		2	.3000	.3040		
4	IT 1	1	.3000	.3100	.30750	.2500E-04
		2	.3100	.3100		
5	JP 1	1	.3050	.3050	.30875	.1892E-04
		2	.3130	.3120		
6	JP 2	1	.2907	.3034	.30015	.5603E-04
		2	.3082	.2983		
7	JP 3	1	.3080	.3040	.30675	.3583E-05
		2	.3080	.3070		
8	JP 4	1	.3110	.3078	.30810	.1572E-04
		2	.3110	.3026		
9	PL 1	1	.2986	.2965	.30540	.8350E-04
		2	.3123	.3142		
10	SE 1	1	.3300	.3160	.32550	.4367E-04
		2	.3300	.3260		
11	SE 2	1	.3104	.3041	.32018	.3130E-03
		2	.3219	.3443		
12	US 1	1	.3152	.3120	.31535	.9630E-05
		2	.3195	.3147		

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-9

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	20.395
CHI-SQUARE(.95,19)	30.148

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

IT 1	ZERO WITHIN-BOTTLE VARIANCE
JP 1	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-9

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	9	.32448303E-02	.36053669E-03
BETWEEN BOTTLES	10	.11034225E-02	.11034225E-03
WITHIN BOTTLES	20	.63232500E-03	.31616250E-04
TOTAL	39	.49805778E-02	

F-CALC = 3.490 F-CRIT(.95;10,20) = 2.348

BETWEEN-BOTTLE VARIANCE IS SIGNIFICANT
TEST SAMPLE IS PRESUMED TO BE INHOMOGENEOUS

ONE-WAY ANOVA CAN NOT BE PERFORMED
PRECISION ESTIMATES FROM TWO-WAY ANOVA

REPEATABILITY VARIANCE	.31616250E-04
REPEATABILITY STD. DEV.	.00562283
BETWEEN-LABORATORIES VARIANCE	.62548611E-04
BETWEEN-LABORATORIES STD. DEV.	.00790877
REPEATABILITY	.01591262
PERMISSIBLE TOLERANCE BETWEEN LABS	.02505097
GRAND MEAN	.30861750
VARIANCE OF THE GRAND MEAN	.90134174E-05

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-7

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS VANADIUM		LAB MEAN	LAB VARIANCE
1	AU 1	1	.1060	.1020	.10200	.8000E-05
		2	.1000	.1000		
2	CA 1	1	.1036	.1025	.10353	.1003E-05
		2	.1045			
3	CA 2	1	.1090	.1095	.10753	.4036E-05
		2	.1056	.1060		
4	IT 1	1	.1100	.1040	.10750	.9000E-05
		2	.1100	.1060		
5	JP 1	1	.1060	.1000	.10650	.2833E-04
		2	.1070	.1130		
6	JP 2	1	.1058	.1034	.10518	.1416E-05
		2	.1056	.1059		
7	JP 3	1	.1030	.1020	.10200	.2000E-05
		2	.1030	.1000		
8	JP 4	1	.1028	.1060	.10418	.2509E-05
		2	.1050	.1029		
9	PL 1	1	.1024	.1013	.10210	.1500E-05
		2	.1010	.1037		
10	SE 1	1	.1000	.1000	.10110	.1640E-05
		2	.1024	.1020		
11	SE 2	1	.1020	.0996	.10235	.3147E-04
		2	.0975	.1103		
12	US 1	1	.1069	.1081	.10708	.7625E-06
		2	.1060	.1073		

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-7

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	20.060
CHI-SQUARE(.95,17)	27.593

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

AU 1	ZERO WITHIN-BOTTLE VARIANCE
CA 1	NUMBER OF BOTTLES OR REPLICATES INCORRECT
SE 1	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-7

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	8	.17714000E-03	.22142500E-04
BETWEEN BOTTLES	9	.75010000E-04	.83344444E-05
WITHIN BOTTLES	18	.16807000E-03	.93372222E-05
TOTAL	35	.42022000E-03	

F-CALC = .893 F-CRIT(.95; 9,18) = 2.456

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-7

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	23.860
CHI-SQUARE(.95,11)	19.681

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE (ALPHA=.05)

SE 2	C-CALC = .343	C-CRIT(4,12) = .326
JP 1	C-CALC = .471	C-CRIT(4,11) = .348

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

JP 1	COCHRAN'S TEST FOR LABORATORY VARIANCE
SE 2	COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-7

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	9	.22073308E-03	.24525897E-04
WITHIN LABS	29	.94596667E-04	.32619540E-05
TOTAL	38	.31532974E-03	

REPEATABILITY VARIANCE	.32619540E-05
REPEATABILITY STD. DEV.	.00180609
BETWEEN-LABORATORIES VARIANCE	.54558802E-05
BETWEEN-LABORATORIES STD. DEV.	.00233578
REPEATABILITY	.00511123
PERMISSIBLE TOLERANCE BETWEEN LABS	.00753379
GRAND MEAN	.10423590
VARIANCE OF THE GRAND MEAN	.63245620E-06

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-6

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS VANADIUM		LAB MEAN	LAB VARIANCE
1	AU 1	1	.0660	.0672	.06280	.1952E-04
		2	.0592	.0588		
2	CA 1	1	.0598	.0599	.05978	.7300E-08
		2	.0597			
3	CA 2	1	.0612	.0608	.06030	.7867E-06
		2	.0592	.0600		
4	IT 1	1	.0600	.0700	.06250	.2500E-04
		2	.0600	.0600		
5	JP 1	1	.0613	.0587	.06015	.1183E-05
		2	.0601	.0605		
6	JP 2	1	.0581	.0606	.05903	.1242E-05
		2	.0590	.0584		
7	JP 3	1	.0598	.0592	.05945	.6333E-07
		2	.0594	.0594		
8	JP 4	1	.0601	.0616	.06100	.5400E-06
		2	.0616	.0607		
9	PL 1	1	.0589	.0578	.05840	.2467E-06
		2	.0587	.0582		
10	SE 1	1	.0608	.0600	.06120	.1387E-05
		2	.0628	.0612		
11	SE 2	1	.0520	.0600	.05380	.2395E-04
		2	.0484	.0548		
12	US 1	1	.0606	.0602	.06030	.2067E-06
		2	.0597	.0607		

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-6

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	24.024
CHI-SQUARE(.95,17)	27.593

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS (ALPHA=.05)

SE 2	BOTTLE- 2	T-CALC = 3.816	T-CRIT(.00227,20) = 3.497
AU 1	BOTTLE- 1	T-CALC = 3.712	T-CRIT(.00238,19) = 3.503
IT 1	BOTTLE- 1	T-CALC = 3.923	T-CRIT(.00250,18) = 3.510
SE 2	BOTTLE- 1	T-CALC = 3.889	T-CRIT(.00263,17) = 3.519

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

AU 1	DOORNBOS' TEST FOR BOTTLE MEANS
CA 1	NUMBER OF BOTTLES OR REPLICATES INCORRECT
IT 1	DOORNBOS' TEST FOR BOTTLE MEANS
JP 3	ZERO WITHIN-BOTTLE VARIANCE
SE 2	DOORNBOS' TEST FOR BOTTLE MEANS

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-6

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	6	.24532143E-04	.40886905E-05
BETWEEN BOTTLES	7	.51725000E-05	.73892857E-06
WITHIN BOTTLES	14	.11605000E-04	.82892857E-06
TOTAL	27	.41309643E-04	

F-CALC = .891 F-CRIT(.95; 7,14) = 2.764

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-6

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	56.955
CHI-SQUARE(.95,11)	19.681

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE (ALPHA=.05)

IT 1	C-CALC = .337	C-CRIT(4,12) = .326	
	BOTTLE- 1 REPLICATE- 2	DIXON'S TEST WITHIN IT 1	
	R10 = 1.000	D-CRIT(4) = .828	
SE 2	C-CALC = .487	C-CRIT(4,12) = .326	
AU 1	C-CALC = .775	C-CRIT(4,11) = .348	

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

SE 2	R = .622	D-CRIT(12) = .479

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

AU 1	COCHRAN'S TEST FOR LABORATORY VARIANCE
SE 2	DIXON'S TEST FOR MEANS AND COCHRAN'S TEST FOR VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

IT 1	BOTTLE- 1	REPLICATE- 2	.0700

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 85-6

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	9	.25919026E-04	.28798918E-05
WITHIN LABS	28	.16982100E-04	.60650357E-06
TOTAL	37	.42901126E-04	

REPEATABILITY VARIANCE	.60650357E-06
REPEATABILITY STD. DEV.	.00077878
BETWEEN-LABORATORIES VARIANCE	.59899752E-06
BETWEEN-LABORATORIES STD. DEV.	.00077395
REPEATABILITY	.00220396
PERMISSIBLE TOLERANCE BETWEEN LABS	.00268813
GRAND MEAN	.05996421
VARIANCE OF THE GRAND MEAN	.76524081E-07

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 79-14

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS VANADIUM		LAB MEAN	LAB VARIANCE
1	AU 1	1	.0368	.0360	.03410	.7400E-05
		2	.0312	.0324		
2	CA 1	1	.0345	.0345	.03453	.0000E+00
		2	.0345			
3	CA 2	1	.0340	.0344	.03370	.3600E-06
		2	.0332	.0332		
4	IT 1	1	.0330	.0380	.03600	.4667E-05
		2	.0370	.0360		
5	JP 1	1	.0359	.0341	.03498	.8225E-06
		2	.0356	.0343		
6	JP 2	1	.0352	.0333	.03355	.1457E-05
		2	.0334	.0323		
7	JP 3	1	.0334	.0332	.03385	.5167E-06
		2	.0348	.0340		
8	JP 4	1	.0344	.0350	.03533	.7825E-06
		2	.0365	.0354		
9	PL 1	1	.0331	.0344	.03318	.7292E-06
		2	.0325	.0327		
10	SE 1	1	.0312	.0316	.03220	.9067E-06
		2	.0328	.0332		
11	SE 2	1	.0344	.0342	.03450	.3000E-05
		2	.0326	.0368		
12	US 1	1	.0345	.0357	.03540	.6000E-06
		2	.0351	.0363		

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 79-14

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	20.009
CHI-SQUARE(.95,19)	30.148

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

CA 1	NUMBER OF BOTTLES OR REPLICATES INCORRECT
CA 2	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 79-14

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	9	.48505250E-04	.53894722E-05
BETWEEN BOTTLES	10	.31297500E-04	.31297500E-05
WITHIN BOTTLES	20	.31345000E-04	.15672500E-05
TOTAL	39	.11114775E-03	

F-CALC = 1.997 F-CRIT(.95;10,20) = 2.348

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 79-14

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	14.098
CHI-SQUARE(.95,10)	18.311

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 79-14

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	11	.50069131E-04	.45517392E-05
WITHIN LABS	35	.63722567E-04	.18206448E-05
TOTAL	46	.11379170E-03	

REPEATABILITY VARIANCE	.18206448E-05
REPEATABILITY STD. DEV.	.00134931
BETWEEN-LABORATORIES VARIANCE	.69761651E-06
BETWEEN-LABORATORIES STD. DEV.	.00083523
REPEATABILITY	.00381855
PERMISSIBLE TOLERANCE BETWEEN LABS	.00358857
GRAND MEAN	.03427021
VARIANCE OF THE GRAND MEAN	.97161321E-07

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-4

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS VANADIUM		LAB MEAN	LAB VARIANCE
1	AU 1	1	.0092	.0088	.00880	.1067E-06
		2	.0088	.0084		
2	CA 1	1	.0112	.0114	.01126	.1363E-07
		2	.0112			
3	CA 2	1	.0088	.0092	.00900	.6933E-06
		2	.0080	.0100		
4	IT 1	1	.0120	.0110	.01225	.9167E-06
		2	.0130	.0130		
5	JP 1	1	.0104	.0109	.01065	.8333E-07
		2	.0104	.0109		
6	JP 2	1	.0095	.0108	.01005	.3100E-06
		2	.0101	.0098		
7	JP 3	1	.0102	.0104	.01045	.3667E-07
		2	.0106	.0106		
8	JP 4	1	.0122	.0110	.01145	.4367E-06
		2	.0118	.0108		
9	PL 1	1	.0112	.0108	.01113	.7825E-06
		2	.0123	.0102		
10	SE 1	1	.0100	.0104	.01000	.1067E-06
		2	.0096	.0100		
11	SE 2	1	.0105	.0117	.01105	.2700E-06
		2	.0112	.0108		
12	US 1	1	.0118	.0114	.01153	.1692E-06
		2	.0119	.0110		

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-4

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	10.752
CHI-SQUARE(.95,17)	27.593

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

CA 1	NUMBER OF BOTTLES OR REPLICATES INCORRECT
IT 1	ZERO WITHIN-BOTTLE VARIANCE
JP 3	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-4

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	8	.32723889E-04	.40904861E-05
BETWEEN BOTTLES	9	.54500000E-06	.60555556E-07
WITHIN BOTTLES	18	.83300000E-05	.46277778E-06
TOTAL	35	.41598889E-04	

F-CALC = .131 F-CRIT(.95; 9,18) = 2.456

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-4

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	16.509
CHI-SQUARE(.95,11)	19.681

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 83-4

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	11	.46364180E-04	.42149255E-05
WITHIN LABS	35	.11762267E-04	.33606476E-06
TOTAL	46	.58126447E-04	

REPEATABILITY VARIANCE	.33606476E-06
REPEATABILITY STD. DEV.	.00057971
BETWEEN-LABORATORIES VARIANCE	.99079594E-06
BETWEEN-LABORATORIES STD. DEV.	.00099539
REPEATABILITY	.00164058
PERMISSIBLE TOLERANCE BETWEEN LABS	.00304646
GRAND MEAN	.01062106
VARIANCE OF THE GRAND MEAN	.90127792E-07

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-12

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS VANADIUM		LAB MEAN	LAB VARIANCE
1	AU 1	1	.0036	.0040	.00340	.2667E-06
		2	.0028	.0032		
2	CA 1	1	.0043	.0045	.00443	.1053E-07
		2	.0045			
3	CA 2	1	.0040	.0044	.00400	.1067E-06
		2	.0036	.0040		
4	IT 1	1	.0050	.0040	.00440	.5067E-06
		2	.0036	.0050		
5	JP 1	1	.0042	.0039	.00428	.3225E-06
		2	.0039	.0051		
6	JP 2	1	.0042	.0042	.00405	.9000E-07
		2	.0042	.0036		
7	JP 3	1	.0038	.0046	.00405	.1433E-06
		2	.0038	.0040		
8	JP 4	1	.0043	.0045	.00450	.2667E-07
		2	.0045	.0047		
9	PL 1	1	.0035	.0036	.00350	.6667E-08
		2	.0034	.0035		
10	SE 1	1	.0039	.0044	.00408	.4917E-07
		2	.0040	.0040		
11	SE 2	1	.0037	.0038	.00390	.2333E-06
		2	.0046	.0035		
12	US 1	1	.0051	.0048	.00488	.2917E-07
		2	.0049	.0047		

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-12

BARTLETT'S TEST FOR HOMOGENEITY OF BOTTLE VARIANCE

CALCULATED STATISTIC	16.061
CHI-SQUARE(.95,17)	27.593

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DOORNBOS' TEST FOR BOTTLE MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR TWO-WAY ANOVA

CA 1	NUMBER OF BOTTLES OR REPLICATES INCORRECT
JP 2	ZERO WITHIN-BOTTLE VARIANCE
SE 1	ZERO WITHIN-BOTTLE VARIANCE

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-12

TWO-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	8	.71350000E-05	.89187500E-06
BETWEEN BOTTLES	9	.12950000E-05	.14388889E-06
WITHIN BOTTLES	18	.36300000E-05	.20166667E-06
TOTAL	35	.12060000E-04	

F-CALC = .713 F-CRIT(.95; 9,18) = 2.456

TEST SAMPLE IS HOMOGENEOUS

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-12

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	20.024
CHI-SQUARE(.95,11)	19.681

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE (ALPHA=.05)

NONE REJECTED

DIXON'S TEST FOR LABORATORY MEANS (ALPHA=.05)

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 19B VANADIUM BY BPHA SPECTOPHOTOMETRIC METHOD
SAMPLE: 76-12

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	11	.74704078E-05	.67912798E-06
WITHIN LABS	35	.53635667E-05	.15324476E-06
TOTAL	46	.12833974E-04	

REPEATABILITY VARIANCE	.15324476E-06
REPEATABILITY STD. DEV.	.00039146
BETWEEN-LABORATORIES VARIANCE	.13432887E-06
BETWEEN-LABORATORIES STD. DEV.	.00036651
REPEATABILITY	.00110785
PERMISSIBLE TOLERANCE BETWEEN LABS	.00129980
GRAND MEAN	.00411489
VARIANCE OF THE GRAND MEAN	.14510341E-07